
(12) UK Patent Application (19) GB (11) 2 064 556 A

- (21) Application No 8011292
- (22) Date of filing 3 Apr 1980
- (30) Priority data
- (31) 100375
- (32) 5 Dec 1979
- (33) United States of America (US)
- (43) Application published 17 Jun 1981
- (51) INT CL³
C08L 33/00 39/06
- (52) Domestic classification
C3M 120 121 123 125
151 201 XX
C3Y B120 B121 B126
B127 B135 B230 B240
B245 B370 E181 F202
- (56) Documents cited
None
- (58) Field of search
C3L
C3M
C3V
- (71) Applicants
The Kendall Company, 1
Federal Street, Boston,
Massachusetts 02101,
United States of America
- (72) Inventor
Kishore Ramanlal Shah
- (74) Agents
Gee & Co., Chancery
House, Chancery Lane,
London WC2A 1QU

(54) Water absorptive polymer composition

(57) A composition capable of absorbing more than 45% of its weight of water without dissolution at room temperature to form a hydrogel is made by blending (1) 40 to 98% of water-soluble poly(vinyl pyrrolidone) with (2) 2 to 60% of a water-insoluble copolymer formed of 50% to 90% based on the total copolymer of a

hydrophobic water-insoluble ethylenically unsaturated monomer, 2 to 12% of an ethylenically unsaturated monomer containing an acid group, and 0 to 50% of a hydrophilic ethylenically unsaturated monomer free from acidic groups. The compositions are useful as dressings, coatings for articles which come into contact with body tissues, and glass which is susceptible to fogging and for controlled release of drugs.

GB 2 064 556 A

SPECIFICATION

Water absorptive composition

This invention relates to a composition capable of absorbing more than 45% of its weight of water without dissolution at room temperature to form a hydrogel and pertains more specifically to an
 5 optically clear blend of a poly-(N-vinyl-2-pyrrolidone) with a water-insoluble copolymer derived from 5C% to 90% by weight, based on the total weight of the copolymer, of a hydrophobic water-insoluble
 ethylenically unsaturated monomer, 2% to 12% by weight of an ethylenically unsaturated monomer
 containing an acid group, and 0 to 50% by weight of a hydrophilic ethylenically unsaturated monomer
 free from acidic groups.

10 It has previously been proposed to insolubilise polymeric N-vinyl lactams such as poly(vinyl
 pyrrolidone) by reaction with water-soluble polymers containing carboxyl groups, the reaction product
 precipitating from solution when the two are mixed, as described in Stoner U.S. Patent 2,901,457. As
 pointed out by Stoner et al. at column 4, lines 56—73, the reaction product there described always has
 15 substantially the same properties and contains the two polymeric components in the same proportions
 regardless of the proportions of the two used to make the product. The compositions of the present 15
 invention, on the other hand, vary in properties and in proportions of components depending upon
 proportions of starting materials. It has also been proposed in O'Driscoll et al. U.S. Patent 3,700,761, in
 Grucza U.S. Patent 3,807,398 and in Le Boeuf et al. U.S. Patent 4,018,853 to make covalently cross-
 20 linked hydrogels by polymerizing hydrophilic methacrylate monomers in the presence of poly(vinyl
 pyrrolidone).

The compositions of the present invention are capable of absorbing more than 45% of their own
 weight of water when immersed in water at room temperature and may absorb even more than ten
 times their weight of water. Despite the absorption of such large amounts of water, the compositions
 retain their coherence and dimensional integrity and do not dissolve; these characteristics make them
 25 particularly useful for several biomedical purposes which require that the hydrogel come into intimate 25
 contact with body tissues or cavities.

The mechanism of interaction between the poly (vinyl pyrrolidone) and the copolymer in the blend
 is not fully understood, but the blend does behave like a physical mixture rather than a chemical reaction
 product in that it can be separated into the two polymeric components by gel permeation
 30 chromatography. The blends are optically clear and substantially free from haziness, indicating that the 30
 blend is homogeneous despite the fact that the poly (vinyl pyrrolidone) is water-soluble and the
 copolymer is water-insoluble. Examination at high magnification under an electron microscope shows
 the presence of microphase domains (4000 Å or less in diameter) of water-insoluble material dispersed
 in the continuous phase of water-soluble poly(vinyl pyrrolidone). The presence of these microphase
 35 domains of the water-insoluble copolymer prevents dissolution of the continuous phase polymer in 35
 water, but unlike covalent cross-linking of polymers does not render the blend non-thermoplastic.
 Instead, the blend possesses the ability to be repeatedly shaped or formed under moderate pressure at a
 temperature as low as 150°C., or in some cases even lower. The shaped or formed composition retains
 its shape at room temperature subject to distortion when swollen with water. The compositions of the
 40 present invention in which the dispersed submicroscopic particles (micro-phase domains) act as 40
 multiple cross-links to prevent dissolution of the hydrophilic continuous phase (which by itself is water-
 soluble), form a new class of hydrogels, distinct from those in which the cross-linking is provided by
 weak cohesive forces, hydrogen bonds, ionic bonds, or covalent bonds.

The water-soluble poly(vinyl pyrrolidone) employed in the compositions of the present invention
 45 may have a molecular weight varying over a wide range from 10,000 to 1,000,000 or more, but those 45
 polymers having molecular weights from 100,000 to 1,000,000 are preferred.

The copolymers which can be employed as blends with the poly(vinyl pyrrolidone) in the
 compositions of the present invention include water-insoluble copolymers of a hydrophobic water-
 insoluble ethylenically unsaturated monomer such as alkyl esters of acrylic or methacrylic acid in which
 50 the alkyl group has from 1 to 16 carbon atoms, styrene, acrylonitrile, vinyl acetate, vinyl butyrate, vinyl 50
 chloride, vinylidene chloride, ethylene, propylene, butylene, butadiene and other polymerizable
 alkadienes, vinylalkyl ethers and vinyl alkyl ketones in which the alkyl group has 3 or more carbon
 atoms. The copolymers also include as another essential monomer an ethylenically unsaturated
 monomer containing an acid group such as a carboxylic, sulfonic, or phosphonic acid group; among
 55 suitable acidic monomers are acrylic acid, methacrylic acid, crotonic acid, maleic acid, 2-sulfo ethyl 55
 methacrylate and 1-phenyl vinyl phosphonic acid. The third monomer, is selected from a group of
 hydrophilic ethylenically unsaturated monomers, possessing a solubility parameter in excess of 11
 [calories/cm³]^{1/2}, free from acidic groups, such as methacrylamide, acrylamide, hydroxyethyl
 methacrylate, diethylene glycol monomethacrylate, triethylene glycol monomethacrylate and glyceryl
 60 methacrylate. 60

In the case of each of the three types of monomers a mixture of two or more individual monomers
 of the same type can be used.

Compatibility or incompatibility of the water-insoluble copolymer with the water-soluble polymer
 of N-vinyl-2-pyrrolidone, in the hydrated form of the blend, that is, its suitability for use in the present

invention, can in each case be readily determined by visual examination of a blend of the two polymers after equilibration in water at room temperature. If the blend is transparent and optically clear and remains so after immersion in water at 20°C without dissolution in the water, it forms a satisfactory hydrogel. If the blend is cloudy or opaque after equilibration in water, or if it dissolves in water at 20°C, the blend made from that copolymer is not satisfactory and possesses poor mechanical properties. For a blend composition to possess satisfactory mechanical properties in the hydrated form, the size of the microphase domains of the terpolymer in the hydrogel should not be greater than 4,000 Å, and preferably should be below about 1,000 Å.

The relative proportions of the different monomers in the copolymer may vary widely; the hydrophobic water insoluble ethylenically unsaturated monomer may amount to 50% to 90% by weight, based on the total weight of copolymer, while the ethylenically unsaturated monomer containing an acidic group may amount to 2% to 12% by weight; the hydrophilic ethylenically unsaturated monomer may amount to 0 to 50% by weight. The exact proportions of the three types of monomers are determined by the hydrophobic-hydrophilic balance required in each case. In many cases, for attainment of this balance the incorporation of 15 to 45% of a hydrophilic monomer is required.

Thus, in the case of one preferred class of copolymers the amount of methyl methacrylate (or styrene or 2-ethylhexyl acrylate) is from 55 to 70% by weight based on the total copolymer weight, the amount of acrylic acid is from 2 to 12% by weight, and the amount of methacrylamide is from 25—43% by weight.

In the case of another preferred copolymer, the amount of *n*-butyl methacrylate is from 65 to 80% by weight based on the total copolymer weight, the amount of acrylic acid is from 2 to 12% by weight, and the amount of methacrylamide is from 15 to 35% by weight.

In the case of still another preferred copolymer, the amount of methyl methacrylate is from 88 to 90% by weight of the total copolymer, while 2-acrylamido-2-methyl propanesulfonic acid, the only other monomer constituent, is from 10—12% by weight. In this case, the presence of a non-acidic hydrophilic comonomer is not essential.

In the case of still another preferred copolymer the amount of *n*-butyl methacrylate is from 50 to 78% by weight of the total copolymer, the amount of acrylic acid is from 2 to 12% by weight, and the amount of hydrophilic *p*-styrene sulfonamide is from 20 to 35% by weight. In another preferred copolymer, the amount of *n*-butyl methacrylate is from 55 to 70% of the total copolymer weight, acrylic acid is from 2 to 12%, and hydroxyethyl methacrylate is from 25 to 43%.

The relative proportions of poly(vinyl pyrrolidone) and of copolymer in the blend vary over a wide range, from 40 to 98% by weight, preferably from 50 to 98%, based on the total weight of the blend, of the former and from 2 to 60% by weight, preferably from 2 to 50%, of the copolymer; optimum proportions of each within the range vary depending upon the particular properties desired in the blend as well as upon the identity of the particular copolymer present in the blend. The greater the proportion of the copolymer in the blend, the lower is the equilibrium water content of the resultant hydrogel. The water content of the PVP-blend hydrogels of this invention can be varied from approximately 30% to 95% or higher by judicious selection of the copolymer and its proportion in the blend. In general, the higher the water content of the hydrogel, the poorer become its mechanical properties.

The blend can be made by mixing together solutions or dispersions of the poly(vinyl pyrrolidone) and of the copolymer in any desired vehicles or solvents which are miscible with each other, then removing the vehicle or solvent, as by evaporation. It may also be possible to blend the polymer and copolymer on a hot roll mill or in an extruder or in other conventional mixing equipment. Shaped articles of the blend can be prepared by casting from a suitable solvent or by a molding process under the influence of heat and pressure.

The thermoplasticity of these hydrogel-forming blends confers on them a special processing advantage over covalently cross-linked synthetic hydrogels. Tailoring of mechanical and physical properties (e.g., water content, solute and water permeability, softness, flexibility, tensile strength) of the hydrogel is readily accomplished by control of the physico-chemical characteristics and the proportion in the blend of the water-insoluble copolymer. Due to these advantages the novel hydrogel compositions of this invention lead themselves to several applications such as burn and wound dressings, coatings for catheters and surgical sutures, soft contact lenses, implants for delivery of medicaments at controlled rates, and other articles coming into intimate contact with body tissues or cavities (e.g., vitreous and corneal prostheses).

These new hydrogel-forming materials can also be used in the manufacture of devices for controlled delivery of drugs which are sparingly soluble in water. When a drug (soluble in the water-insoluble copolymer) is incorporated in these hydrogels, it remains dispersed in hundreds of thousands of "depots" of water-insoluble domains. The delivery rate of the drug consequently is governed by partition coefficient of the drug in the aqueous and non-aqueous phases, membrane geometry, and the size and the number of the dispersed domains. An advantage of such a device is that a mechanical failure or a pin-hole would not cause any increase in the delivery rate of the drug.

A non-medical use of the novel compositions of this invention is for coating glass surfaces, such as inner sides of automotive and aircraft windshields, to render them non-fogging. This is accomplished by casting from a suitable solvent a thin coating of a blend composition, such as that described in Example

19, on a glass surface. Formation of the polymeric blend coating can also be accomplished by a spray of its dilute solution in a suitable solvent. The coating has a good adhesion to glass, is colorless, optically clear, and non-fogging upon exposure to hot, moist air.

The following specific examples are intended to illustrate more fully the nature of the present invention without acting as limitations upon its scope.

EXAMPLES 1 — 13

Each of the copolymers of these Examples was prepared by conventional solution polymerization procedure by dissolving the desired proportions of monomers in a suitable solvent and by employing as an initiator of polymerization a small amount (0.2—0.4% by weight of monomers) of a free radical generator such as azobisisobutyronitrile or 2-*t*-butylazo-2-cyanopropane. Polymerization was carried out at 80—95°C to a high degree of conversion. The composition of the copolymerization mixtures is described in Table I. Copolymers of the Examples 1 to 4 were isolated from the reaction mixture by precipitation into methanol, collected by filtration, and dried at 100°C under vacuum, whereas, the copolymer of Example 5 was isolated by removal of the volatiles by heating in vacuum at 100°C.

TABLE I

Reaction Ingredients	Example No.				
	1	2	3	4	5
<u>Comonomers — Grams</u>					
Methyl methacrylate	65	—	—	90	—
Methacrylamide	30	30	15	—	30
Styrene	—	65	—	—	—
Acrylic acid	5	5	5	—	5
<i>n</i> -Butyl methacrylate	—	—	80	—	—
2-Acrylamido-2-methylpropane sulfonic acid	—	—	—	10	—
2-Ethylhexyl acrylate	—	—	—	—	65
<u>Solvents — Milliliters</u>					
Ethanol	100	100	100	—	100
Dioxane	100	100	100	—	—
N,N-Dimethylformamide	—	—	—	100	100

Each of the blend compositions of these Examples was prepared by dissolving in N,N-dimethylformamide the desired proportions of the water-insoluble copolymer and poly(vinyl pyrrolidone) (Grade K-90, mol.wt., 36,000) to obtain a solution containing 10—15% by weight of the polymeric blend. The solution of the blend was then heated at 100°C under vacuum to evaporate the solvent, leaving a mass of optically transparent blended solid material. The blend, which was thermoplastic, was pressed into a disc in a mold heated at 150°C. The molded disc was placed in deionized water for 72 hours, during which time it absorbed water and swelled to form a hydrogel. The compositions of the blends, their physical appearance, and the equilibrium water content of their hydrogels are described in Table II.

TABLE II

Example No.	Blend of Composition		Physical Appearance		Equilibrium water content Weight %
	Copolymer of Example No.	Parts by Weight of PVP (K-90) per 100 parts of the Blend	Dry Form	Hydrated Form	
6	1	70	Transparent, solid	Transparent, strong	68
7	1	90	"	"	91
8	2	70	"	"	58
9	2	90	"	"	80
10	3	90	"	Translucent, coherent	90
11	4	90	"	Transparent, coherent	84
12	5	70	"	Transparent, strong	77
13	5	90	"	"	90

EXAMPLES 14—15

5 A 20.8 g (0.10 mole) portion of phosphorous pentachloride was placed in a 500 ml. round-bottomed flask and 17.4 g (0.084 mole) of pulverized *p*-sodium styrenesulfonate was added slowly with ice bath cooling. The mixture was stirred cautiously with a magnetic stirrer. After 30 min. it was heated under reflux at 50—60°C for 2 hrs. The product was cooled and poured into 100 g of crushed ice and extracted with 100 ml of chloroform. The organic layer containing *p*-styrenesulfonyl chloride was separated, washed several times with distilled water, and dried over magnesium sulfate.

10 The chloroform solution (100 ml) containing *p*-styrenesulfonyl chloride was added with mechanical stirring into 340 ml of 30% ammonium hydroxide (specific gravity 0.90) while cooling with ice over a period of about 30 min. The mixture was heated to 50°C for 5 hrs. under a reflux condenser and then cooled to room temperature.

The organic layer was separated, dried over anhydrous magnesium sulfate, and then evaporated to dryness to yield a solid white powder of crude *p*-styrenesulfonamide, which was purified by recrystallization from ethanol-water mixture to yield about 6.0 g of the sulfonamide m.p. 130—132°C.

15 The infra red spectrum of the sulfonamide showed absorptions at 3350 and 3260 cm⁻¹ (NH stretching), 1600 cm⁻¹ (aromatic c = c) 1305 and 1160 cm⁻¹ (S = O stretching), and 840 cm⁻¹ (*p*-disubstituted benzene, 2 adjacent CH wagging).

20 A copolymer of 62% *n*-butyl methacrylate, 30% *p*-styrenesulfonamide prepared as described above, and 8% acrylic acid was prepared in the usual way, as described in Examples 1—13, employing 33% concentration of the monomers in a mixture of ethyl alcohol and dioxane. The copolymer was purified by precipitation of the reaction mixture in chloroform, then isolated by filtration and dried *in vacuo* at 100°C.

25 Blends of the copolymer with poly(vinyl pyrrolidone) (PVP, Grade K-90, mol. wt. 360,000) were prepared as described in Examples 1 to 13, by dissolving the copolymer and PVP in dimethylformamide and subsequently evaporating the solvent at 100°C *in vacuo*. Blends containing 10% and 30% by weight of copolymer, respectively, the balance being poly(vinyl pyrrolidone) in each case, were found to be optically transparent solids. Molded discs of the two blends, prepared as described in Examples 1 to 13, were found to absorb water and form transparent hydrogels containing 84.6% and 62.5% water by weight, respectively, when equilibrated with deionized water at room temperature for 72 hours.

EXAMPLES 16—19

35 Hydroxyethyl methacrylate (HEMA) was purified by extracting (4 to 6 times) a 1:1 solution of the polymer in water with petroleum ether, then saturating the aqueous monomer solution with sodium chloride, and extracting the monomer with chloroform. The combined chloroform extracts were dried over anhydrous magnesium sulfate and the solution distilled *in vacuo* (0.1 mm on Hg) using cuprous chloride as inhibitor. The monomer fraction distilled over at 70—82°C.

A copolymer of 52% butyl methacrylate, 40% HEMA and 8% acrylic acid was prepared in the usual way, as described in Examples 1—13, employing 25% concentration of the monomers in a mixture of ethyl alcohol and dioxane.

- Optically clear blends of the copolymer in varying proportions with poly (vinyl pyrrolidone) (PVP, Grade K-90, mol. wt. 360,000) were prepared as described in Examples 1—13 by dissolving the copolymer and PVP in dimethylformamide and subsequently evaporating the solvent at 100°C *in vacuo*. Approximately 8—12 mil thick sheets of the blends were compression molded, after which they were equilibrated in deionized water at room temperature for 72 hours. It was found that blends containing 70, 80 and 90% by weight, respectively, of PVP formed hydrogels containing 75.8%, 82.3% and 88.9% by weight of water, respectively.

EXAMPLES 20—26

- A copolymer of 62% butyl methacrylate, 8% acrylic acid, and 30% methacrylamide was prepared by the same general method as described in Examples 1—13, and optically clear blends of the resultant copolymer with varying amounts of the same poly(vinyl pyrrolidone), Grade K-90, were prepared as described in Examples 16—19.

- It was found that a linear relationship existed between the proportion (10 to 40%) of the copolymer in the blend and equilibrium water content of the hydrogels as shown in column A of Table III below. In order to take into account the change in the properties of the PVP in the blend due to incorporation of the copolymer, hydration of the PVP fraction alone was calculated assuming that swelling of the copolymer in water is negligible as shown in the last column of Table III. Once again it was found that equilibrium water uptake of the PVP fraction was inversely proportional to the amount of copolymer in the blend.

TABLE III

Blend Composition			Hydrogel Compositions		
Copolymer Wt. %	PVP Wt. %	A*	B*	C*	100xW _{H₂O} A x 100
					W _{PVP} +W _{H₂O} A+C % H ₂ O in Hydrated PVP
10	90	83.5	16.5	14.85	84.90
15	85	79.1	20.9	17.765	81.67
20	80	77.7	22.3	17.84	81.33
25	75	69.6	30.4	22.80	75.32
30	70	64.3	35.7	24.99	72.01
35	65	61.7	38.3	24.895	71.25
40	60	55.3	44.7	26.82	67.34

$$A^* = \frac{100 \times W_{H_2O}}{W_{Blend} + W_{H_2O}}$$

$$B^* = \frac{100 \times W_{Blend}}{W_{Blend} + W_{H_2O}}$$

$$C^* = \frac{100 \times W_{PVP}}{W_{Blend} + W_{H_2O}}$$

- The blends of the present invention possess the properties of thermoplasticity, fusibility, and solubility in organic solvents as well as hydratability. But while they retain the thermoplasticity, fusibility, and solubility in organic solvents of the PVP portion of the blend, they exhibit varying hydration characteristics of the PVP portion depending upon the amount of copolymer present.

CLAIMS

1. Composition capable of absorbing more than 45% of its weight of water without dissolution at room temperature to form an optically clear hydrogel and consisting essentially of an optically clear blend of (1) 40 to 98% by weight, based on the total weight of the blend, of a water-soluble polymer of N-vinyl-2-pyrrolidone, having a molecular weight of at least 10,000 and (2) 2 to 60% by weight of a water-insoluble copolymer derived from (A) 50 to 90% by weight, based on the total weight of the copolymer, of a hydrophobic water-insoluble ethylenically unsaturated monomer, (B) 2 to 12% by weight of an ethylenically unsaturated monomer containing an acid group, and (C) from 0 to 50% by weight of a hydrophilic ethylenically unsaturated monomer free from acidic groups. 5
2. A composition as claimed in Claim 1 in which 15 to 45% by weight of the copolymer (2) is derived from the monomer (C). 10
3. A composition as claimed in Claim 1 or 2 in which the monomer (A) is selected from alkyl esters of acrylic or methacrylic acid in which the alkyl group has from 1 to 16 carbon atoms, styrene, acrylonitrile, vinyl acetate, vinyl butyrate, vinyl chloride, vinylidene chloride, ethylene, propylene, butylene, butadiene and other polymerizable alkenes, vinyl alkyl ethers and vinyl alkyl ketones in which the alkyl group has 3 or more carbon atoms. 15
4. A composition as claimed in any preceding Claim in which the monomer (B) contains a carboxylic, sulfonic or phosphoric group.
5. A composition as claimed in Claim 4 in which the monomer (B) is selected from acrylic acid, methacrylic acid, crotonic acid, maleic acid, 2-sulfo ethyl methacrylate and 1-phenyl vinyl phosphonic acid. 20
6. A composition as claimed in any preceding claim in which the monomer (C) is selected from methacrylamide, acrylamide, hydroxyethyl methacrylate, diethylene glycol monomethacrylate, triethylene glycol monomethacrylate and glyceryl methacrylate.
7. A composition as claimed in any preceding claim in which said blend contains by weight from 50 to 98% of the polymer (1) and from 2 to 50% of the copolymer (2). 25
8. A composition as claimed in Claim 2 in which the copolymer (2) is derived from 55 to 70% by weight, based on the total weight of the copolymer, of a monomer selected from methyl methacrylate, styrene, and 2-ethylhexyl acrylate, 2 to 12% by weight of acrylic acid and 25 to 43% by weight of methacrylamide. 30
9. A composition as claimed in Claim 2 in which the copolymer (2) is derived from 65 to 80% by weight based on the total weight of the copolymer of *n*-butyl methacrylate, 2 to 12% by weight of acrylic acid, and 15 to 35% by weight of methacrylamide.
10. A composition as claimed in Claim 1 in which the copolymer (2) is derived from 88 to 90% by weight, based on the total weight of the copolymer, of methyl methacrylate and 10 to 12% by weight of 2-acrylamido-2-methyl propanesulfonic acid. 35
11. A composition as claimed in Claim 2, in which the copolymer (2) is derived from 50 to 78% by weight, based on the total weight of the copolymer, of *n*-butyl methacrylate, 2 to 12% by weight of acrylic acid, and 20 to 35% by weight of *p*-styrene sulfonamide.
12. A composition as claimed in Claim 2 in which the copolymer (2) is derived from 55 to 70% by weight, based on the total weight of the copolymer, of *n*-butyl methacrylate, 2 to 12% by weight of acrylic acid, and 25 to 43% by weight of hydroxyethyl methacrylate. 40
13. A composition as claimed in any preceding Claim in which the polymer (1) has a molecular weight of from 10,000 to 1,000,000.
14. A catheter or suture coated with a composition as claimed in any preceding claim. 45
15. A composition as claimed in any preceding claim and having a drug incorporated therein.
16. A glass sheet coated with a composition as claimed in any one of Claims 1 to 13.
17. The features as herein disclosed, or their equivalents, in any novel selection.

New claims or amendments to claims filed on 9 July 1980

50 Superseded claims —

New or amended claims:—

1. Composition capable of absorbing more than 45% of its weight of water without dissolution at room temperature to form an optically clear hydrogel and consisting essentially of an optically clear blend of (1) 40 to 98% by weight, based on the total weight of the blend; of a water-soluble polymer of N-vinyl-2-pyrrolidone, having a molecular weight of at least 10,000 and (2) 2 to 60% by weight of a water-insoluble copolymer derived from (A) 50 to 90% by weight, based on the total weight of the copolymer, of a hydrophobic water-insoluble ethylenically unsaturated monomer, (B) 2 to 12% by weight of an ethylenically unsaturated monomer containing an acid group, and (C) from 15% to 45% by weight of a hydrophilic ethylenically unsaturated monomer free from acidic groups. 55